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Immobilization of Bromocresol Purple in Inorganic-Organic Sol-Gel Thin Film with Presence of anionic and non-ionic surfactants

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Abstract

Sol-gel materials known as organically modified silicates (ORMOSILs) offer interesting features such as chemical and mechanical stability. In this paper VTES (vinyltriethoxysilane) and TEOS (tetraalkoxysilane) are mixed in 3:1 ratio. Sol-gel solution was prepared by hydrolysis process of precursors by using ethanol as solvent. After a while a pH-sensitive indicator bromocresol purple (BCP) and surfactant were incorporate into the sol-gel mixture. The percentage of sodium dodecyl sulfate (SDS) and polyethylene glycol (PEG) which act as surfactant were varied to observe the effect of improving host material's nanostructure as well as the interaction between BCP and sol-gel matrices. The absorption peak of the BCP dye changed significantly in the presence of surfactant compared to pure VTES: TEOS mixture (control) in the range of 400 to 450nm. The presence of BCP dye in the sol-gel mixture can be determined via FTIR spectrum with a =C–H stretch in aromatics observed at 3100-3000 cm^{-1} which represented the aromatic of the BCP structure. The addition of BCP and surfactant had influenced the FTIR spectra of VTES: TEOS sol-gel materials. Addition of an anionic surfactant to the sol-gel mixtures was found to increase the BCP dye and the sol-gel matrices interaction, thus reducing the dye's tendency to leach. This work shows that sol-gel derived matrices yield dyes with sufficient rigid environment and addition of the surfactant helps to improve the interaction of filler matrices. The anionic SDS shows better leaching resistant compared to non-ionic PEG surfactant. Results of this study offer an attractive possibility to optimize the doped sol gel matrices to be used as sensing material in aqueous condition.

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1. Introduction

Over the decades, the response and mechanism of numerous dyes in different matrices of polymers and sol-gels have been investigated[1]. Sol-gels have gained widespread interests for applications in optical sensing. However, a type of sol-gel materials known as Organically Modified Silicates (ORMOSILs) offer interesting features, such as chemical and mechanical stability[2]. The term "sol-gel" refers to a chemical process where metallic or semimetallic alkoxide precursors or their derivatives form composites at moderate temperatures through a chemical reaction. It is reported that the combination of organic vinyltriethoxysilane (VTES) and inorganic tetraethoxysilane (TEOS) can be used to make protective, hard and crack-free coating on substrates[3, 4]. Organic part of the hybrid materials can improve adhesion between coating and polymer substrate whilst the inorganic part can increase the hardness of the coating and remains unaltered during sol-gel process, acting as network modifiers that terminate the silica network. In ORMOSILs, the interconnection of organic and inorganic moieties in the matrices results in microstructure changes, improvement of density, flexibility and optical properties[5]. Typical processes for preparing ORMOSILs are cohydrolysis and co-condensation from a mixture of tetralkoxysilane (TEOS) and an organic group of the organotrialkoxysilane such as of vinyltriethoxysilane (VTES). The nonreactive organic groups do not undergo hydrolysis or condensation, but remain unaltered during the sol–gel process and act as a network modifier that terminates the silicate networks by react with the remaining active site after the hydrolysis or condensation process. In addition to chemical and mechanical properties of the ORMOSILs material, other important parameter is their optical properties for sensor application such as excellent sensitivity, short response time and low limit of detection when doped with a colorimetric or fluorimetric indicator[4].

Wide range of organic dyes are suitable due to several factors, namely high surface area of the host matrix, porosity of the material formed and low temperature of the sol-gel method. In recent years, great attention has been put in the encapsulation of sensitive dyes into porous sol-gel materials[6,7]. The ability of bromocresol purple to detect ammonia in aqueous solution makes it as one of the materials with high potential to be used as sensing material in ammonium detection and as for that reason Bromocresol Purple is being chosen for this study. However, BCP dye could potentially leach out from the host matrix which could undermine its stability[1]. Therefore, a surfactant was introduced to improve the dye-sol gel matrix interaction. Formation of mesostructures of silica matrix with high silica porosity is achievable by using surfactants and it was found that the resulting mesostructures could efficiently host sensing molecules. One notable example could be found in the work of Avnir and co-workers[8] who reported that chemical and spectral properties of co-doped pH indicators were affected by immobilization of several surfactants in sol–gel matrices.

The main objective of this study is to observe the effect of surfactant in reducing the rate of leaching of the dye as well as investigating its effect on physical properties of sol gel film. Bromocresol Purple (BCP), an organic dye, was incorporated into VTES and TEOS precursors with different surfactant ratios of SDS and PEG. The sol-gel precursor mixtures were then drop-casted on slide glasses to form thin films and subsequently undergone heat treatment. BCP doped sol-gel matrices absorption spectral and physical properties of the matrices were analyzed. Finally sol-gel film's leaching behavior was studied.

Nomenclature

VTES	Vinyltriethoxysilane
TEOS	Tetralkoxysilane
BCP	Bromocresol purple
PEG	Polyethylene glycol
SDS	Sodium dodecyl sulfate

2. Experimental

2.1 Materials

Tetraethoxysilane (TEOS 98% purity, Fluka Chemical), vinyltriethoxysilane (VTES 98% purity, Tokyo Chemical Industry Co), bromocresol purple (BCP, Bendosen Laboratory Chemicals), sodium dodecyl sulfate (SDS 99% purity, Sigma Aldrich) and polyethylene glycol 600 (PEG, Sigma Aldrich) were used as received.

2.2 Preparation of thin films

Precursors of TEOS, VTES and their molar ratio mixtures (3:1) were prepared by hydrolysis in acid catalyzed ethanolic medium. The molar ratio of precursor to ethanol and deionized water is 1:4:2 respectively. Precursors were mixed with ethanol before being added with deionized water of pH 5 one hour later. The solution was then mildly stirred overnight at room temperature to ensure homogeneous mixing. Next, 0.02% of BCP was added to either SDS or PEG of variable percentages of 0.5%, 1%, 1.5%, 2% and2.5% with respect to the total volume of the prepared sol and stirred for one hour. All mixtures produced yellowish color. Thin film was fabricated on 8 x 25 mm slide glass by dropping an average of 80µl of the mixture which then slowly moved across the glass to produce flat films. Samples were placed inside an oven for heat treatment at a temperature of 60ºC for 24 hours.

2.3 Characterization

Chemical compositions of the immobilized BCP with different type of surfactant were characterized by using Perkin-Elmer RXI double beam Fourier transform infrared (FTIR) with a resolution of 2 cm^{-1} to determine the presence of each surfactant and to verify its reaction with silica network. Absorption spectra for all samples were measured using UV/VIS Spectrometer (Perkin-Elmer Lambda 25) where the samples were placed into a cuvette cell filled with 2.5 mL deionized water while the hardness of the film were measured by nanoindentention nanotest MML (platform 2) to observed the change of mechanical properties under the presence of different surfactant.

3. Results and Discussion

3.1 FTIR measurement analysis

Fig. 1 shows the FTIR spectra of the immobilized BCP and the pure (control) sol-gel materials. There is no significant spectral difference between immobilized BCP and the pure sol-gel because the silica network dominates the spectra. The presence of BCP dye can be determined by the FTIR spectrum where a =C–H stretch in aromatics is observed at 3100-3000 cm^{-1} [11] which is typical representation of the aromatics of BCP structure. Asymmetric stretching of Si-O-Si bands are represented by transmission band around 770 cm^{-1}, 1044 cm^{-1} and 1184 cm^{-1} respectively. Transmission band around 880 cm^{-1} represents Si-OH bond, Si-C bond at 1409 cm^{-1}, C=C bond at 1600 cm^{-1} whilst 3065 cm^{-1} belongs to C-H bond [3]. Both C=C and C-H bonds can be influenced by the organic part of VTES. Addition of BCP influences the FTIR spectra of VTES:TEOS sol-gel materials, which shows that a reaction has occured between the dopant and the silica network.

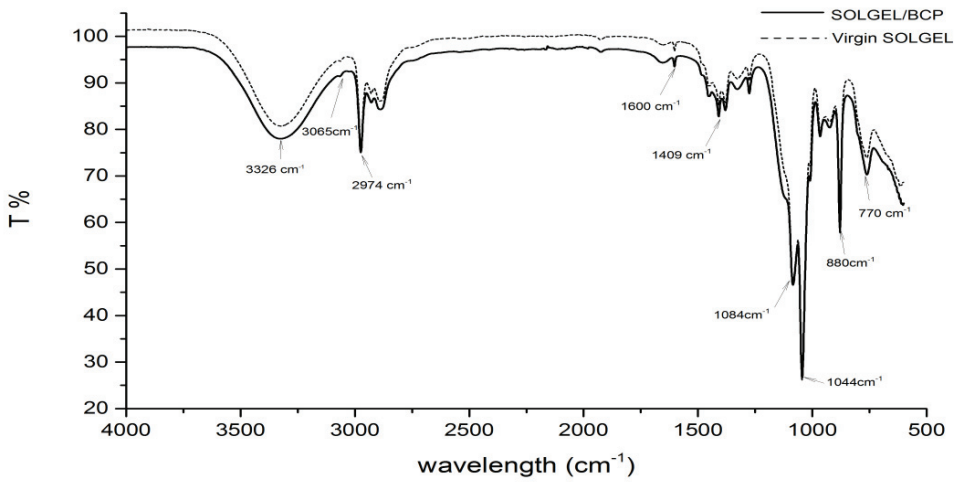

Fig.1. FTIR spectra of immobilized BCP and virgin sol-gel

3.2 Optical characterization

3.2.1 Absorption spectra in the presence of surfactant

Absorption spectra were analyzed to verify the presence of BCP and to determine the effect of surfactant toward silica network. Different ratios of SDS, and PEG surfactants (0.5%-2.5%) versus its absorption spectral are presented in Fig. 2 and Fig. 3 respectively. By examining the absorption spectra at around λmax = 430–435 nm, absorption peak for each formulations can be determined, which was due to the yellowish color of the coated film, which indicates the presence of BCP. It was found that increasing surfactant's concentration (PEG and SDS) increases the absorbance where 2.5% concentration gives the maximum value. This result implies that increasing surfactant's concentration will increase the number of binding sites available in the surfactant.

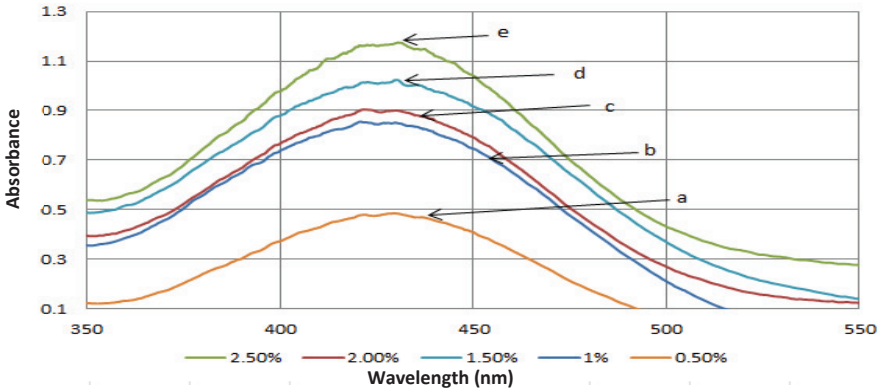

Fig. 2. Absorption spectra of immobilized BCP/PEG at different volume ratio of PEG:(a) 0.5 %, (b) 1%, (c) 1.5% (d) 2%, and (e) 2.5%.

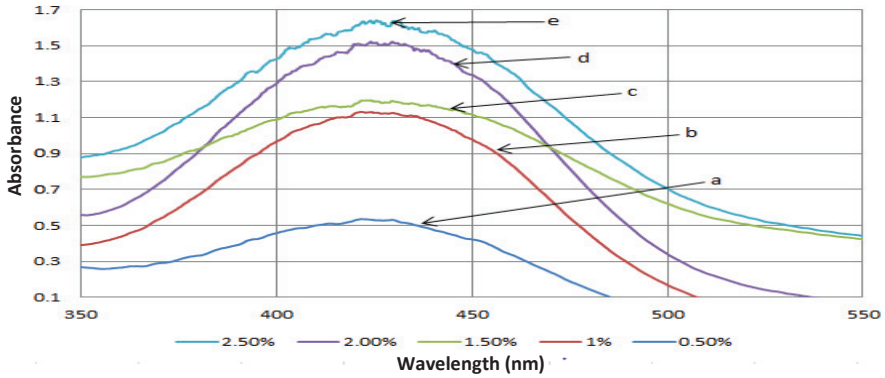

Fig.3. Absorption spectra of immobilized BCP/SDS at different volume ratio of SDS:(a) 0.5 %, (b) 1%, (c) 1.5% (d) 2%, and (e) 2.5%.

Nonetheless, SDS shows higher reading compared to PEG with an absorbance value of 1.63 as oppose to 1.17 for PEG. Similar behavior can also be observed in Fig. 4.

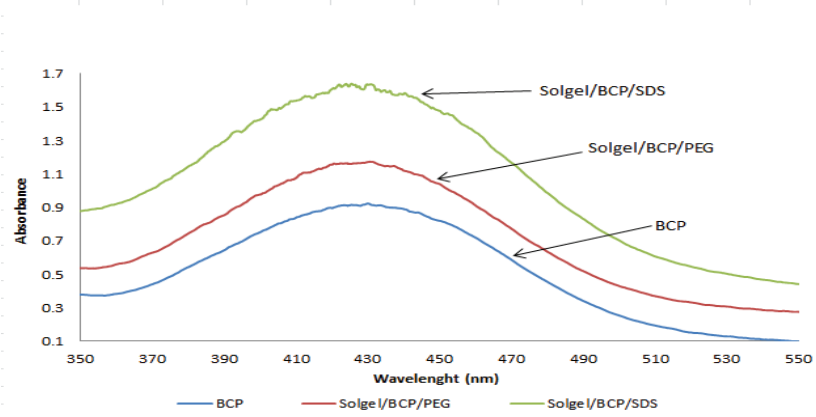

Fig. 4. Absorption spectra of immobilized BCP, BCP/PEG and BCP/SDS in sol-gel matrix

Fig. 4 shows the comparison between PEG, SDS and a reference solution (without surfactant). In general, the presence of surfactant increases absorbance value. This would be caused by the modification of the silica structure which increases its porosity, hence increasing the capacity of the silica network (host) to be loaded with BCP. It is observed that anionic SDS surfactant shows the most significant change, indicated by the highest absorbance value. Ionic surfactant gave a better absorbance value than non-ionic surfactant due to it strong ionic charge which impart the repulsive forces during synthesis process hence controls to increase the porosity within the silica networks[9].

3.2.2 Effect of surfactant on dye leaching

The effect of surfactant on leaching of BCP was studied (Fig. 5). All the sample were exposed to a pH 4 leachate solution for about 5 hours, and then tested for their absorbent to observe the percentage of leaching reduction. The lowest leaching of BCP molecules from thin films was observed when SDS surfactant was used with leaching percentage of 23%. Based on Figure 5, leaching percentages of BCP from the thin film silica matrix are arranged in

the following order : immobilized BCP>BCP/PEG>BCP/SDS. By incorporating surfactant, the leaching rate has decreased where SDS gives the lowest leaching percentage. This is due to strong interaction between BCP molecules and the silica host network [9].

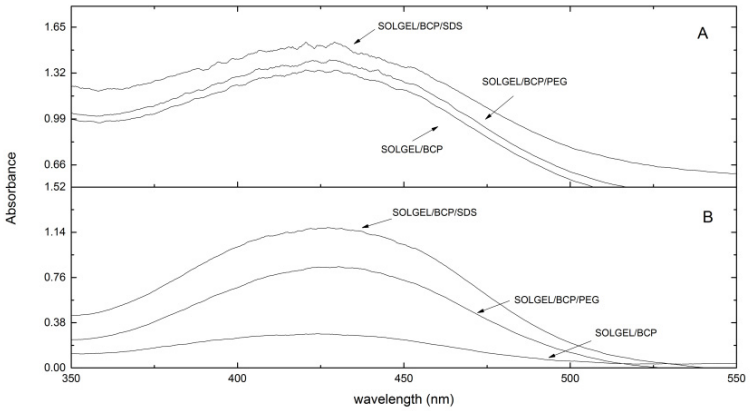

Fig. 5. Absorption spectra of immobilized BCP, BCP/PEG and BCP/SDS in sol-gel matrix (A) Before being exposed to leachate (B) after 5 hours exposure

3.3 Nanomechanical properties

Nanomechanical properties have been observed by nanoindentation testing to understand the effect of surfactant on the mechanical properties of the film. A berkovich tip being used as the indenter whereby a maximum load of 3mN for each indentation has been deployed. Fig. 6 shows the representative load–displacement curves of immobilized BCP, BCP/PEG and BCP/SDS in sol-gel matrix under the same conditions. It can be observed that no 'pop-in' events occur in all the samples, suggesting that all the indentation were done on homogenous surface thickness. 'Pop-in' phenomenon may refer to plastic deformation characterized by multiple discontinuities at certain penetration depths[10].

Hardness value for immobilized BCP, BCP/PEG and BCP/SDS are demonstrated in Table 1. The average hardness value obtained for immobilized BCP is 0.14 ± 0.02 GPa, which is the highest, compared to other samples. The hardness result suggests that the presence of surfactant reduces the film hardness. The reason of the decreasing film hardness is due to the interaction between silica network and BCP dyes which improves upon surfactant addition as surfactant lower the tension between BCP dyes and silica network while promoting better interaction between them. Reducing hardness of the material will reduce surface brittleness hence eliminating surface cracking as a result of improved film stability.

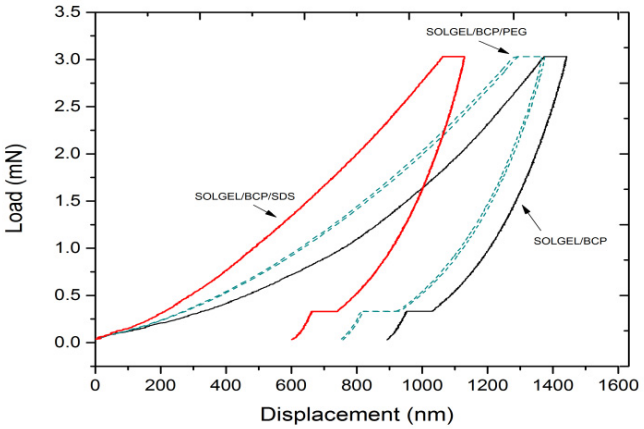

Fig. 6. Representative load–displacement curves from nanoindentation of immobilized BCP, BCP/PEG and BCP/SDS in sol-gel matrix

Table 1. Reduce modulus and hardness of Sol gel/BCP, Sol gel/BCP/PEG and Sol gel/BCP/SDS obtained by nanoindentation

Material	E_r (GPa)	Hardness (GPa)
SOLGEL/BCP	1.85 ± 0.26	0.14± 0.02
SOLGEL/BCP/PEG	1.47 ± 0.05	0.10± 0.04
SOLGEL/BCP/SDS	1.16 ± 0.31	0.08 ± 0.02

4. Conclusions

A monolithic BCP immobilized thin films were fabricated using organic-inorganic derived sol-gel matrices, which entrapped a pH indicator namely Bromocresol Purple (BCP), in the presence of anionic SDS and non-ionic PEG surfactants.This work shows that the nature of the matrix does not only affect the optical properties of BCP but also increases the stability of the dye. The sol-gel derived matrices with the presence of surfactant provide the dye with an improved sufficient rigid surrounding environment. The best thin film obtained was the BCP/SDS which showed the highest absorbance and the lowest leaching rate. The surfactant has enhanced electrostatic attraction between BCP and silica host matrix which resulted in improved film stability.

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References

1. Malins, C., Butler, T. M. and MacCraith, B.D. (2000) "Influence of the surface polarity of dye-doped sol-gel glass films on optical ammonia sensor response", Thin Solid Films, vol 368, pp. 105-110.
2. Chan, Z., Ai'mei, L., Xiao, Z., Miao, F., Juan, H. and Honbing, Z. (2007) "Microstructures and properties of ORMOSIL comprising methyl, vynil, and γ-glycidoxypropyl-substituted silica", *Optical Materials*, vol. 29, pp.1543-1547.

3. Eo, Y.J., Kim, D.J., Bae, B.S., Song, K.C., Lee, T.Y. and Song, S.W. (1998) "Coatings of Tetraethylorthosilicate (TEOS) /Vinyltri-ethoxysilane (VTES) Hybrid Solution on Polymer Films", Journal of Sol-Gel Science and Technology, Vol.13, pp.409-413.
4. Korent,S.M., Lobnik, A. and Mohr, G.J. (2007). "Sol-gel-based optical sensor for the detection of aqueous amines", Analytical and Bioanalytical Chemistry. Vol. 387, p. 2863-2870.
5. Avnir, D., Braun, S., Lev, O, Levy, D. and Ottolenghi, M. (Eds.) (1994) "Sol-gel Optics-Processing and Application", Kluwer, Boston, vol23:539-582
6. Zaggout, R. (2006). "Entrapment of phenol red pH indicator into a sol-gelmatrix," Materials Letters, vol. 60, no. 8, pp. 1026–1030.
7. El-Nahhal, I. M., Zourab, S. M., and El-Ashgar, N. M. (2001). "Encapsulation of phenolphthalein pH-indicator into a sol-gel matrix," Journal of Dispersion Science and Technology, vol. 22, no. 6, pp. 583–590.
8. Sanchez-Barragan, I., Costa-Fernandez, J.M., and Sanz-Medel, A. (2005). "Tailoring the pH response range of fluorescent-based pH sensing phases by sol–gel surfactants co-immobilization", Sensors and Actuators B Chemica, vol 107 , pp.69-76.
9. Nizam M. El-Ashgar, Ahmed I. El-Basioni, Issa M. El-Nahhal, Shehata M. Zourob, Taher M. El-Agez, and Sofyan A. Taya. (2012). "Sol-Gel Thin Films Immobilized with Bromocresol Purple pH-Sensitive Indicator in Presence of Surfactants," ISRN Analytical Chemistry, vol. 2012, 11 pages, doi:10.5402/2012/604389
10. Tasi, C.H., Tseng, Y.C., Jian, S.R. et al. (2015). "Nanomechanical properties of Bi2Te3 thin films by nanoindentation," Journal of Alloys and Compounds, vol. 619, pp. 834–838.
11. Tavakkoli, H., Ghaemi, A., Mostofizadeh, M. (2014) "Synthesis and Evaluation Catalytic Efficiency of Perovskite-Type Oxide Nanopowders in Removal of Bromocresol Purple from Aqueous Solution" International Journal of Scientific Research in Knowledge, vol 2, p 340-351